UPGRADING OF DISTILLATE PRODUCTS FROM COAL LIQUEFACTION AND COAL/BITUMEN COPROCESSING

Michael F. Wilson

CANMET, Energy Research Laboratories, Energy, Mines and Resources Canada
555 Booth Street, Ottawa, Ontario K1A 0G1

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INTRODUCTION

Upgrading of heavy coal liquids involves first-stage hydrotreating with the objective of removing heteroatomic species, particularly nitrogen, which can be a serious poison for catalysts in second-stage hydrocracking or FCC. Hydrotreating also achieves molecular weight reduction and increases the hydrogen content of the coal liquid prior to cracking to lighter products suitable for use as transportation fuels.

A major problem in coal liquids upgrading is deactivation of hydrotreating catalysts through fouling of the catalyst surface. Deactivation has been attributed to the strong adsorption of certain feedstock nitrogen and oxygen containing components at acidic catalyst sites, as well as fouling by asphaltenic materials and polynuclear aromatic hydrocarbons. The adsorbed species are believed to act as precursors for the formation of carbonaceous deposits which result in loss of surface area and plugging of catalyst pores. These aspects of coal liquids upgrading have been adequately reviewed by Derbyshire (1). Previous work was undertaken by Chevron Research Company, notably Sullivan and Frumkin (2,3), who identified feedstock properties which were found to most influence the ease of upgrading: boiling point distribution, distillation end-point, heteroatom content and hydrogen content.

The objectives of this work were to undertake experimental hydrotreating of two gas oil feedstocks derived respectively from liquefaction of coal and coprocessing coal/bitumen. The purpose was to compare the upgradeability of the coal derived liquids for use as transportation fuels and to identify solutions to the problem of catalyst fouling and deactivation.

EXPERIMENTAL

The feedstocks used in the program were: Nedol process spent donor solvent, supplied by Sumitomo Metal Mining Co. Ltd., Ichikawa, Japan, and a CANMET coal/bitumen coprocessed heavy gas oil fraction. The latter feedstock was derived from coprocessing 70% Cold Lake bitumen and 30% Forestburg coal. The feedstocks represent two different sources and processing technologies for production of transportation fuels from coal. In both cases the materials require extensive upgrading to produce distillates which meet the required specifications as liquid fuels. The boiling range of both feedstocks was between 200°C-550°C. Approximately 2 wt % of the Nedol process spent donor solvent boiled above 525°C, and the amounts of asphaltenes and preasphaltenes were found to be 4.15 wt % and 0.86 wt % respectively. For the coprocessed gas oil, the +525°C fraction was 1.4 wt % and asphaltenes and preasphaltenes were 1.68 wt % and 0.11 wt %. Since the sulphur content of the spent donor solvent feedstock was low, 3 wt % butanethiol was added to maintain MoS_2 based catalyst activity during screening, following the procedure of Inoue et al. (4).

An automated microreactor unit was used to hydrotreat the coal liquid feedstocks and study the effects of catalyst deactivation. Time on stream catalyst deactivation runs were carried out to establish the extent of fouling by problematical feedstock components. A fixed bed stainless steel tubular reactor, 0.305 m long, 0.635 cm I.D., was operated in the continuous upflow mode. The catalyst bed was 0.14 m long and of volume 4.50 cm³. The catalyst was presulphided in situ with a mixture of 10% H_2S

in H_2. Operating conditions for carrying out the catalyst deactivation experiments were: temperature 380°C, hydrogen pressure 10.3 MPa (1500 psig), LHSV 1.00, and hydrogen flowrate 1000 L H_2/L liquid feed (5500 scf/bbl).

Hydrotreating experiments were also carried out using a Robinson-Mahoney gradientless stirred tank reactor (5) to determine conversion of heteroatoms and aromatics in coprocessed liquid. The reactor is a continuous flow unit equipped with an annular catalyst basket and internal recycle impeller. The internal reactor volume was approximately 50 cm³ and the catalyst bed 6.0 cm³. The catalyst was first presulphided using a mixture of 3 wt % butanethiol in diesel fuel and was then de-edged for three days (72 h) using the same feedstock. De-edging conditions were: temperature 380°C, hydrogen pressure 10.3 MPa (1500 psig), WHSV 0.75 and gas flowrate 1000 mL H_2/mL liquid feed. The coprocessed heavy gas oil was introduced into the reactor and the internal recycle impeller rate was set at 2500 rpm. For each of the catalysts tested, the operating temperatures were 300°C, 340°C, 360°C and 380°C at WHSV 0.75. Three Ni-Mo catalysts were used: AKZO KF-153S, CANMET CER 20 and CANMET CER 24. The physical properties of the catalysts are presented in Table 1.

RESULTS AND DISCUSSION

Feedstock Properties
Figure 1 compares the heteroatom and aromatic content of the two feedstocks. The coprocessed liquid had a significantly lower aromaticity, i.e., $f_a = 0.40$ compared with 0.58 for the spent donor solvent. There was also a large difference in elemental sulphur. Coprocessed gas oil had a very high sulphur content, i.e., 2.29 wt %, compared with 0.069 wt % for the spent donor solvent. The amounts of elemental nitrogen were about the same, but the coprocessed material had a somewhat lower oxygen content, i.e., 0.80 wt % compared with 1.60 wt % for the Nedol coal liquid. Further characteristics of coprocessed products are given by Rahimi et al. (6).

Catalyst Deactivation Runs For Hydrotreating Coal Liquids - Nitrogen Conversion (Effect of time on Stream)
Commercial catalyst AKZO KF-153S was used to hydrotreat the coal derived liquids at the prescribed operating conditions for between 200-300 h time on stream. Since sulphur was added to the spent donor solvent and oxygen content was difficult to analyze, the two parameters monitored were nitrogen and aromatics conversion. The catalyst was de-edged using the coal derived liquid feedstocks over 80 h time on stream. Plots of per cent nitrogen conversion versus catalyst time on stream are presented in Fig. 3. For both feedstocks the nitrogen conversion declined during the initial 80 h period. The commercial catalyst continued to show a steady decline in activity for the spent Nedol process donor solvent up to 200 h. For this feedstock the catalyst initially demonstrated a nitrogen conversion of greater than 80%. The effect of time on stream on nitrogen conversion in the coprocessed liquid, also plotted in Fig. 3, shows an interesting phenomenon which is observed over the first 200 h. The nitrogen conversion appears to decline during the first 80 h of the experimental run, but then recovers and rises to a maximum at approximately 130 h. Thereafter the catalyst activity appears to stabilize. An examination of this phenomenon suggests that during hydrotreating there is a transition from one type of catalytic site to another. Thus, at first, deactivation of active sites appears to occur, then in situ regeneration of the catalyst appears to take place. This may be the result of accumulation of H_2S in the reactor over the first 80 h, leading to regeneration of the catalyst. For the coprocessed gas oil, between 200-300 h time on stream, the activity of the AKZO catalyst appears to decline slowly.

Aromatics Conversion (Effect of Time on Stream)
The other indicator of catalyst deactivation relates to hydrogenation of aromatic type ring structures in the feedstocks. The fraction of aromatics, f_a, in the feed and products was determined by ¹³C NMR. Figure 4 plots f_a versus time on stream for hydrogenation of the feedstocks over the commercial

catalyst. For Nedol process spent donor solvent, the catalyst showed a steady rate of deactivation over 200 h. In the case of coprocessed gas oil, the AKZO catalyst showed good hydrogenation activity with some scatter of experimental data but little deactivation. It is important to note that the cyclical deactivation/regeneration phenomenon shown in Fig. 3 for the HDN reaction was not observed in this case. This suggests that different catalytic sites are involved for the hydrogenation reactions and these were unaffected throughout the experimental run.

Determination of Heteroatom and Aromatics Conversion in Coprocessed Gas Oil Using a Gradientless Reactor
To determine meaningful conversion data for hydrotreating the coprocessed heavy gas oil feedstock, experimental runs were carried out using the gradientless stirred tank reactor (5). An insufficient amount of Nedol process spent donor solvent was available, therefore it was not possible to carry out corresponding determinations on that material. Because the gradientless reactor permits determinations under isothermal conditions with uniform reactant concentrations, it provides a means of accumulating reliable feedstock conversion data. Hydrotreating catalysts used were the high surface area commercial catalyst AKZO KF-153S and CANMET catalysts CER 20 and CER 24 for aromatics and heteroatom conversion respectively (see Table 1).

Determination of Nitrogen and Sulphur Conversion in Coprocessed Heavy Gas Oil
Figure 5(i) presents plots of per cent nitrogen conversion in coprocessed gas oil versus reaction temperature over catalysts AKZO KF-153S and CER 24. Both catalysts had high surface areas and reasonably good agreement is observed for nitrogen removal. At the maximum operating temperature, 380°C, the nitrogen conversion was approximately 80%. Plots of per cent sulphur conversion for the coprocessed gas oil versus reaction temperature are presented in Fig.5 (ii). Again, high conversions (approximately 94%) were obtained at the maximum operating temperature. It is also shown that, at low sulphur conversions, a significant difference in conversion was found for the two catalysts tested. It is apparent from the general trends of the two curves plotted, that catalyst AKZO KF-153S had a higher chemical reaction rate at the lower temperatures. However, as the temperature is increased to the maximum, the two plots are seen to converge to a single point. This phenomenon is attributed to the HDS reaction being diffusion controlled at the higher temperatures. Catalyst AKZO KF-153S has a significantly higher surface area and pore volume than CER 24. However, this advantage is lost when the rate of diffusion of sulphur containing molecules into the catalyst pores becomes rate determining and it is observed that the sulphur conversion became the same for both catalysts.

Determination of Aromatics Conversion in Coprocessed Gas Oil
Input of additional hydrogen into the coprocessed liquid should facilitate second-stage upgrading to naphtha and middle distillates by improving product quality and reducing the amount of coke formed on cracking catalysts. Plots of per cent conversion of coprocessed gas oil aromatic carbon (^{13}C NMR) over catalysts AKZO KF-153S and CER 20 versus reaction temperature are presented in Fig. 5(iii). Again, the curvature and convergence of the two plots indicates that aromatics hydrogenation over the Ni-Mo catalysts became diffusion controlled at the higher operating temperatures. These diffusion control effects in coprocessed gas oil were also confirmed by constructing Arrhenius plots for the hydrotreating reactions. As expected, the plots showed curvature in the high temperature region.

CONCLUSIONS
Time on stream hydrotreating runs showed that an overall higher rate of catalyst deactivation occurred during upgrading of the product from coal liquefaction. The limited amount of deactivation shown by the coprocessed liquid is considered acceptable for commercial operations. However, it was also shown that, at the higher operating temperatures, reactions were diffusion controlled.

Figure 2 compares final properties of hydrotreated products in terms of heteroatom and aromatics

content. It is shown that the regenerated Nedol process donor solvent had a significantly higher aromatic content (46.0%) than the corresponding coprocessed liquid product (25.0%). This difference is also reflected in the product atomic H/C ratios which were 1.32 and 1.69 respectively. Concerning nitrogen content, which is a key performance indicator for hydrocracking operations, both coal liquid products had about the same concentration, i.e, 1000-1200 ppm. No final measurements of elemental oxygen content were made, but experience has shown that oxygen is easier to convert. Similarly, Fig. 2 shows that sulphur conversion is not a problem. In summary, since hydrocracking operations usually require a final product nitrogen specification of approximately 10 ppm, and further hydrotreating was shown to consume excessive amounts of hydrogen, problems are anticipated in meeting the hydrocracking specification for both feedstocks. It is therefore concluded that fluid catalytic cracking is a better option than hydrocracking for converting coal derived and coprocessed heavy gas oils to lighter products.

ACKNOWLEDGEMENTS

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Table 1 - Physical Properties of Ni-Mo Hydrotreating Catalysts

Catalyst	Surface area (m^2/g)	Pore volume (cm^3/g)
AKZO KF-153S	286	0.43
CANMET CER 20	166	0.21
CANMET CER 24	230	0.34

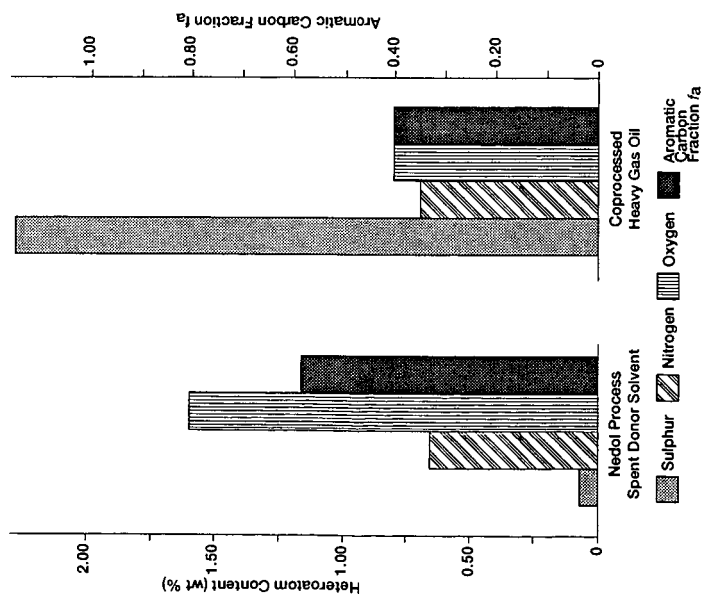Figure 2 - Heteroatom and Aromatic Content of Hydrotreated Products

Figure 1 - Heteroatom and Aromatic Content of Coal Derived and Coprocessed Liquid Feedstocks
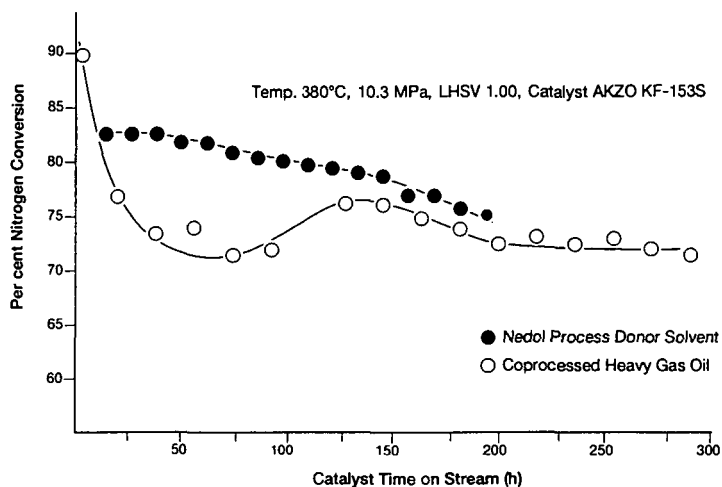
Figure 3 - Nitrogen Conversion in Hydrotreated
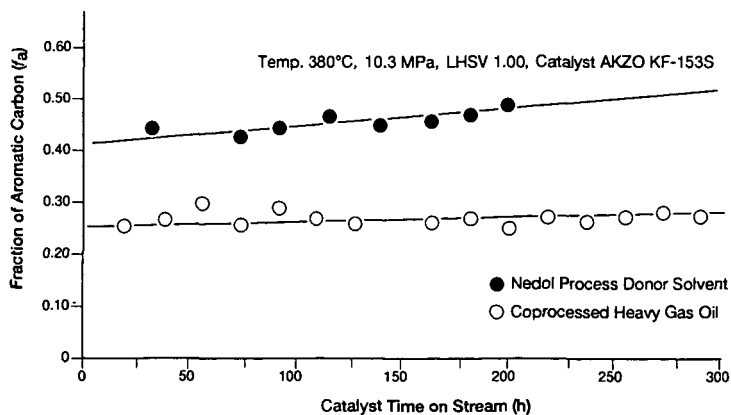Products as a Function of Time on Stream

Figure 4 - Hydrotreated Product Aromacity
as a Function of Time on Stream

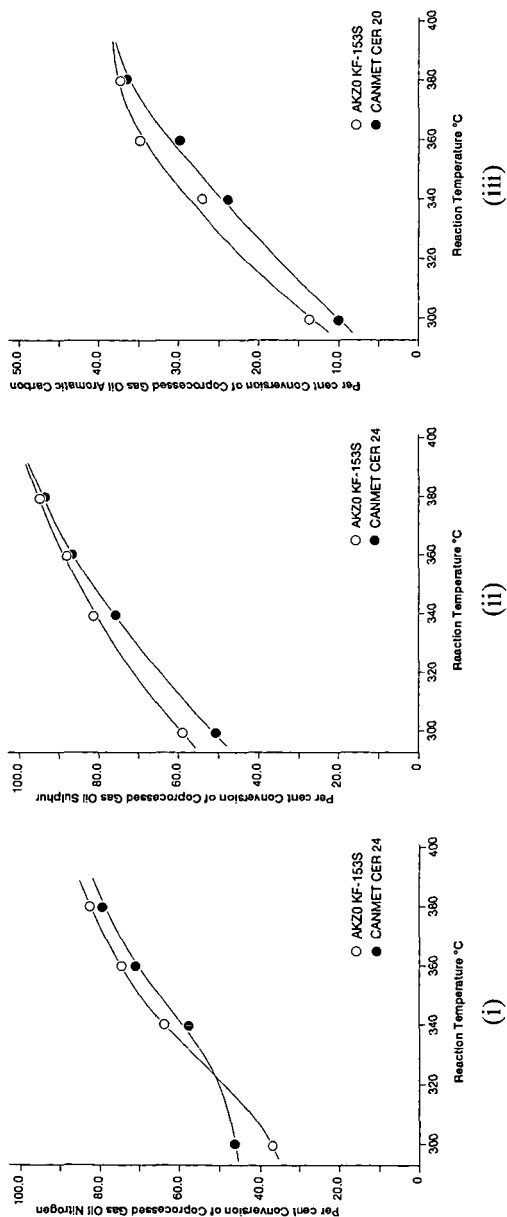Hydrogen Pressure 10.3 MPa, WHSV 0.75

Figure 5 - Effect of Temperature on Conversion of Coprocessed Gas Oil Nitrogen, Sulphur and Aromatic Carbon over Ni-Mo Catalysts Using a Gradientless Reactor